Thermal Expansion and Temperature Dependence of Young's Modulus of Single Crystal of Hexagonal Cobalt

Thermal Expansion and Temperature Dependence of Young's Modulus of Single Crystal of Hexagonal Cobalt*

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(Received August 23, 1967)

Synopsis

By using a dilatometer and a vibrator-controlled oscillator system, the thermal expansion and Young's modulus of single crystals of hexagonal cobalt in a long cylindrical form were measured at temperatures ranging over from −100° to 350°C. From the measured values and the known values of compressibility, the elastic parameter, the elastic constant and the rigidity modulus were calculated. The thermal expansion coefficient, Young's modulus and the rigidity modulus were also calculated for polycrystal, the results of which were in good agreement with the values measured for the polycrystal specimens prepared from the melt.

I. Introduction

The elastic parameter S_{ij} and the elastic constant C_{ij} of hexagonal close-packed cobalt have been obtained by Honda and Shirakawa[1] from room-temperature Young's modulus E by a static bending technique, and Mckskimin[2] has reported C_{ij} obtained by an ultrasonic pulse echo technique. These are the data only available so far, though they are not consistent with each other, because probably of small single crystal specimens about 1 cm in length which were cut out of a bulk in both experiments.

To obtain more accurate data, in the present case, long cylindrical single crystal specimens were prepared by Bridgman's method[3], and it was seen that the crystal would grow to the length of about 10 cm when the cooling rate was properly adjusted[4]. By this method, single crystals of cobalt with different

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* The **1319th** report of the Research Institute for Iron, Steel and Other Metals, and the **15th** report of the Foundation: The Research Institute of Electric and Magentic Alloys. This paper was presented at the 1965 spring and autumn meetings of the Japan Inst. Metals. Reported in Japanese in J. Japan Inst. Metals, **31** (1967), 25.

** The Foundation: The Research Institute of Electric and Magnetic Alloys.

(1) K. Honda and Y. Shirakawa, Sci. Rep. RITU, **A-1** (1949), 9.

(2) H.J. Mckskimin, J. Appl. Phys., **26** (1955), 406.

(3) M. Yamamoto, Sci. Rep. Tôhoku Imp. Univ., **29** (1940), 112; J. Japan Inst. Metals, **4** (1940), 368.

(4) After the contribution of this paper, H.T. Hudson has reported that cylindrical cobalt single crystals were similarly obtained by Tammann-Bridgman's method (Rev. Sci. Instr., **37** (1966), 881).

orientations could be prepared, and E of these specimens was measured at various temperatures below the transformation point. The principal elastic parameter S_{ij} was determined from the measured value of E by using the compressibility κ, from which C_{ij} and the rigidity modulus G were calculated. Measurements of Young's modulus were also made with quasi-isotropic specimens prepared by slow cooling of melt, the results of which were compared with the calculated values.

As for the anisotropy of thermal expansion, only Bibring and Sebilleau (1955)[5] have dealt with the expansion coefficient $\alpha_{//}$ in the hexagonal orientation and $\alpha_{\perp}$ in a perpendicular direction which were calculated from the results of X-ray reflection of the powdered specimen. So, in the present case the thermal expansion coefficient α was measured with the above-mentioned single crystal specimens, and the values of $\alpha_{//}$ in the c axis and $\alpha_{\perp}$ perpendicular to the c axis were derived.

II. Single crystal specimens and method of measurement

1. Single crystal specimens

The single crystal specimens of cobalt were the same as those used in the measurements of the anisotropy in electrical resistivity and of the magnetoresistance effect[6], the size being 6–11 cm in length and about 2 mm in diameter. The stereographic projections of the specimens are shown in Fig. 1, and the angles between the cylindrical axis and the c axis of the specimens are shown in Table 1.

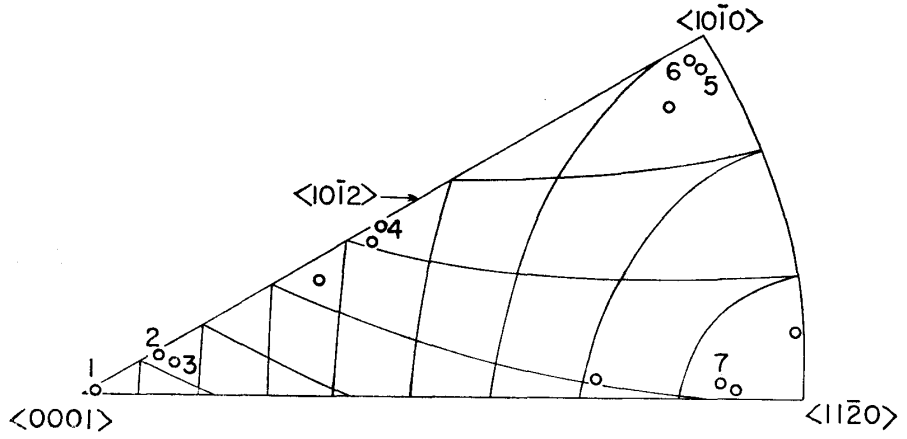

Fig. 1. Stereographic projection of orientations of single crystals of cobalt (Specimens: Nos. 1-7).

2. Method of measurements

The measurement of thermal expansion was carried out at temperatures ranging from −100° to 350°C by means of the Super-Invar vertical dilatometer[7]

(5) H. Bibring and F. Sebilleau, Rev. Met., **52** (1955), 569.
(6) H. Masumoto, H. Saitô and M. Kikuchi, J. Japan Inst. Metals, **30** (1966), 885; Sci. Rep. RITU, **A-18** Supple. (1966), 84.
(7) H. Masumoto and T. Kobayashi, Sci. Rep. RITU, **A-2** (1950), 856.

Table 1. Angle between the c axis and the cylindrical axis of specimens.

No.	Angle from c axis (degr.)	
1	2.06	near <0001>
2	13.00	—
3	16.00	—
4	43.40	near <10$\bar{1}$2>
5	80.95	near <10$\bar{1}$0>
6	84.20	〃
7	82.80	near <11$\bar{2}$0>

and the ordinary horizontal dilatometer, by which were determined the mean linear thermal expansion coefficients at −100°, 20° and 350°C. The natural frequency (700 ~ 1000c/s) of the specimens was determined by means of the vibrator-controlled oscillator system[8], and the density was measured by ordinary weighing method in water. Thus, the value of E was calculated from the measured values of natural frequency, expansion coefficient and density.

III. Experimental results and considerations

1. Thermal expansion

The measurement of thermal expansion was performed at the above-mentioned temperatures on four specimens with orientations nearest to (0001), (10$\bar{1}$2), (10$\bar{1}$0) and (11$\bar{2}$0) as shown in Fig. 2. As seen from the figure, the thermal expansion vs. temperature curve for each specimen is almost linear. The values of $\alpha_{//}$ and $\alpha_{\perp}$ in the principal axis and the value of α of a polycrystal specimen which was calculated from the above results increase linearly with temperature as shown in Fig. 3. The value of $\alpha_{//}$ is fairly high compared with the value of $\alpha_{\perp}$, its rate of increase with temperature being about three times as large as that of the latter. In the same figure is shown in the thermal expansion coefficient α_C of the polycrystal specimen which was calculated from the values of $\alpha_{//}$ and $\alpha_{\perp}$, and the measured values α_M agree fairly well with the calculated values α_C. The dotted line in the figure is based on the data of Bibring and Sebilleau[5] obtained with the powdered specimen by X-ray analysis, in which the value of α is generally higher than the present one, probably due to the use of a powdered specimen and to an indirect method in the determination of α. The mean values for $\alpha_{//}$, $\alpha_{<10\bar{1}2>}$, $\alpha_{\perp}$ ($\langle 10\bar{1}0\rangle$, $\langle 11\bar{2}0\rangle$) and α_C at −100°, 20° and 350°C are shown in Table 2. The relation between the calculated α values and crystal orientations of cobalt is given in Fig. 4, in which the values marked with × indicate the calculated ones for the polycrystal specimen.

(8) Y. Shirakawa and I. Oguma, J. Japan Inst. Metals, **24** (1959), 63.

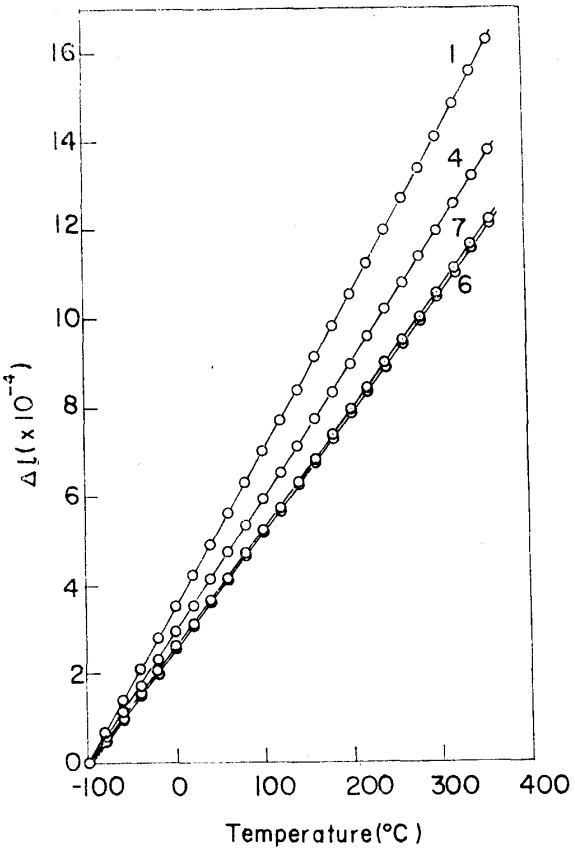

Fig. 2. Thermal expansion Δl of single crystals of cobalt.

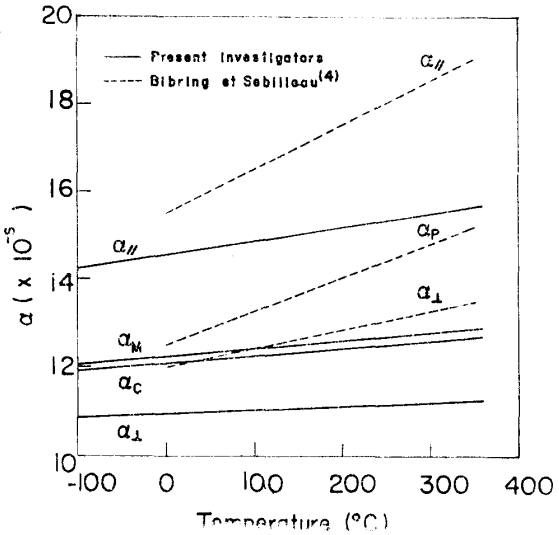

Fig. 3. Calculated thermal expansion coefficient α of the single crystal and the polycrystal of cobalt.

2. Young's modulus

Fig. 5 shows the relation between Young's modulus E of single crystal and temperature, in which E is clearly anisotropic. However, since E in an arbitrary direction cannot be determined from these observed values, it was determined by

Table 2. Calculated values of thermal expansion coefficient α: Young's modulus E and rigidity modulus G and their temperature coefficients e and g.

	α ($\times 10^{-6}$)			E ($\times 10^{12}$dyn/cm^2)	G	e ($\times 10^{-5}$)		g ($\times 10^{-5}$)	
	− 100°C	20°C	350°C	20°C		−50°C ~ 200°C	200°C ~ 350°C	−50°C ~ 200°C	200°C ~ 350°C
<0001>	14.26	14.62	15.61	2.13	0.624	− 52.10	−137.80	− 63.80	−119.70
<10$\bar{1}$2>	12.85	12.95	13.70	1.69	0.741	− 74.60	−114.90	− 39.70	−129.70
<10$\bar{1}$0>	10.86	10.97	11.30	1.75	0.622	− 33.55	−116.70	− 60.65	−119.90
<11$\bar{2}$0>	10.85	10.96	11.29	1.74	0.622	− 37.30	−118.82	− 60.00	−116.00
polycrystal	11.94	12.14	12.71	1.75	0.648	− 43.40	−115.90	− 49.78	−125.10

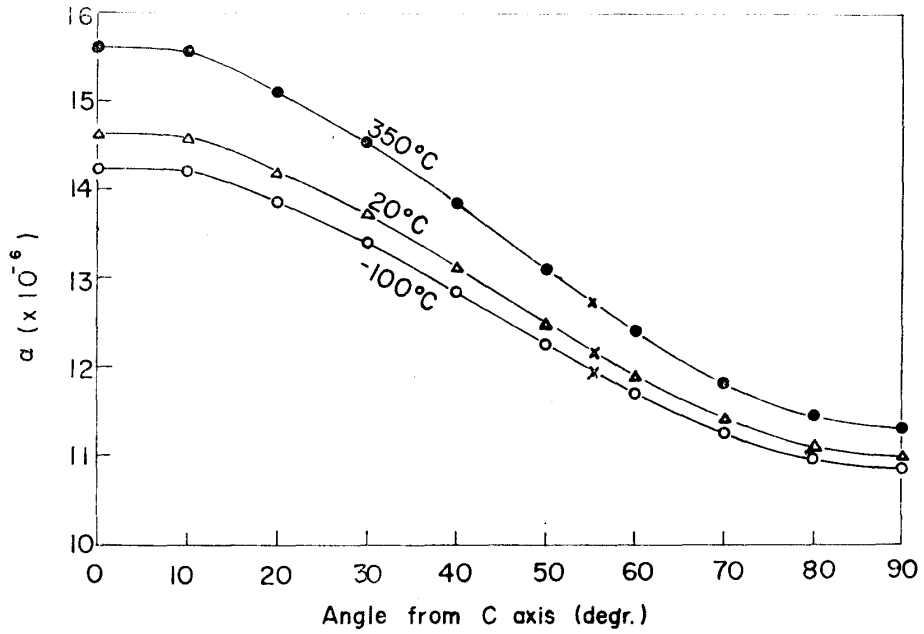

Fig. 4. Relation between calculated thermal expansion coefficients and crystal orientations of cobalt.

the following equation[9] for the hexagonal crystal:

$$\frac{1}{E} = S_{11}(1-\gamma^2)^2 + S_{33}\gamma^4 + (2S_{13}+S_{44})\gamma^2(1-\gamma^2), \qquad (1)$$

where S_{ij} is the elastic parameter, γ the direction cosine of the inclination of the cylindrical axis to the c axis. So, if S_{11}, S_{33} and $(2S_{13}+S_{44})$ are obtained from the observed E by the least square method, E in an arbitrary direction can be calculated from the above equation. The temperature dependence of S_{11}, S_{33} and $(2S_{13}+S_{44})$ and of E at various angles from the c axis and the relation between orientation

(9) W. Voigt, *Lehrbuch der Kristallphsik*, B.G. Teubner, Leipzig (1910), 746.

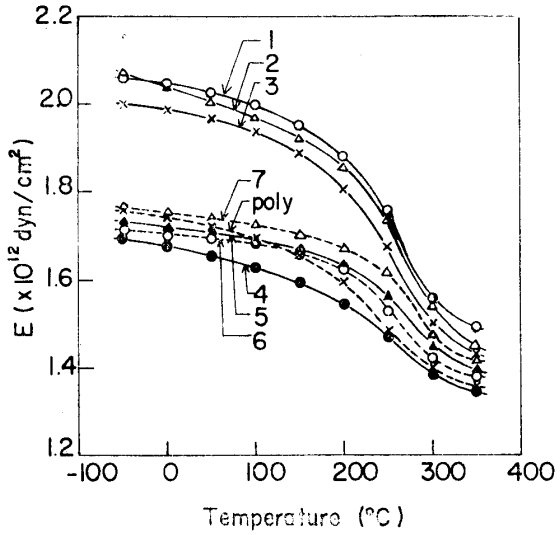

Fig. 5. Temperature dependency of Young's modulus E for the single crystal and the polycrystal of cobalt.

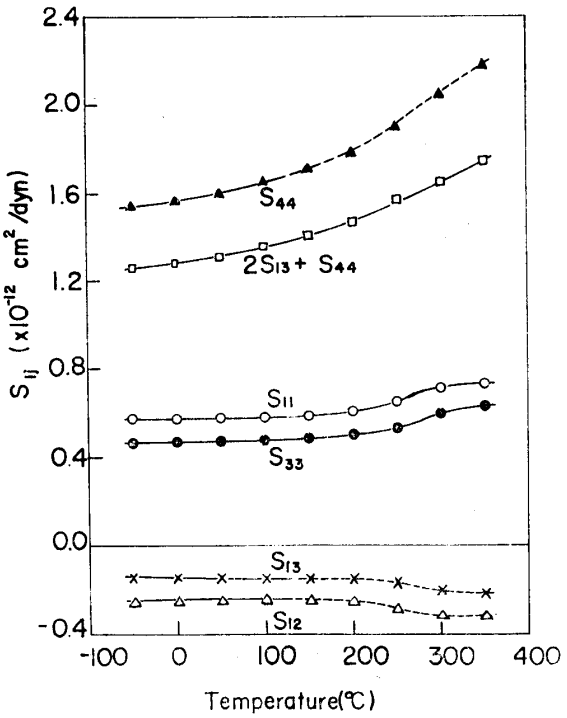

Fig. 6. Elastic parameter S_{ij} of cobalt calculated with volume compressibility κ by Tatsumoto[14].

and E at various temperatures in the $(10\bar{1}0)$ plane are shown in Figs. 6, 7 and 8, respectively. As can be seen from Figs. 7 and 8, E decreases with rising temperature and has a maximum in the c axis at any given temperature; with increasing deviation from the c axis, E begins to decrease rapidly and has a minimum in the orientation of about 50°; E increases slightly near the perpendicular direction.

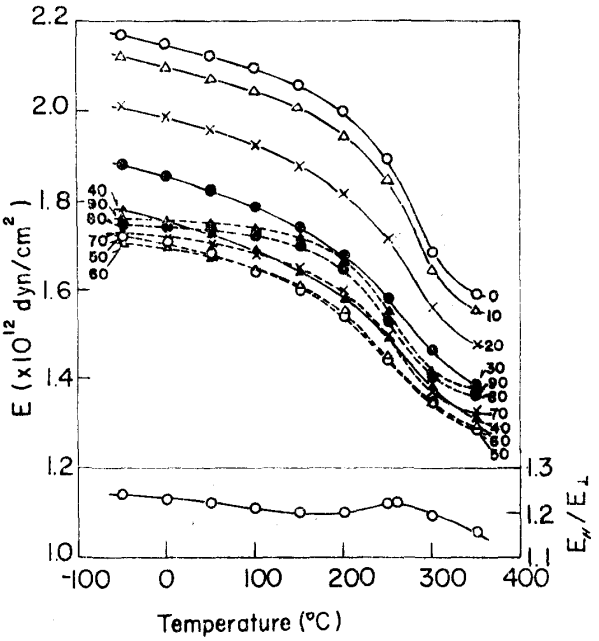

Fig. 7. Calculated Young's modulus E in various directions of single crystals and elastic anisotropy $E_{//}/E_{\perp}$ of cobalt.

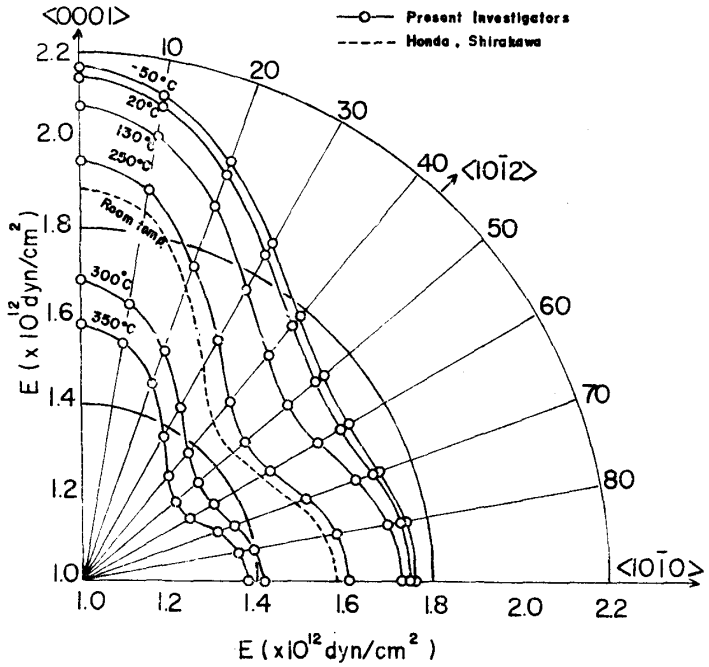

Fig. 8. Young's modulus E in the $(10\bar{1}0)$ plane of hexagonal cobalt calculated with the elastic parameter S_{ij} and also with the result of K. Honda and Y. Shirakawa[1].

The data of Honda and Shirakawa shown in Fig. 8 are much smaller than the present results, which may be attributed to the low accuracy of measurement due to the small size of specimens and to the static measurement. The variation in E with temperature is almost the same in $\langle 10\bar{1}0\rangle$ as in $\langle 11\bar{2}0\rangle$. Fig. 7 also shows a curve of $E_{//<0001>}/E_{\perp<0001>}$ vs. temperature, in which E has a maximum at about 260°C, at

which the sign of the magnetic anisotropy constant reverses[10]. The value of $E_{//<0001>}/E_{<0001>}$ at room temperature is 1.22 as shown in Table 2, in agreement with the result of Honda and Shirakawa, while the value at 350°C is 1.15. The orientation dependence of E at room temperature and that of mean temperature coefficient in the temperature ranges of −50° to 200°C and 200° to 350°C are also shown in Table 2.

Young's modulus for the polycrystal specimen can be computed by substituting 1/3 and 1/5 as mean values of the direction cosines γ^2 and γ^4 in Eq. (1), respectively[1]. Figure 9 shows the calculated values and the measured values for the polycrystal specimen prepared by slow cooling of melt, both values being in good agreement.

Next, the compressibility κ is expressed by Eq. (2), and since the second term is zero for the isotropic crystal, Eq. (3) will be obtained:

$$\kappa = S_{11} + S_{12} + S_{13} - \gamma^2 (S_{11} + S_{12} - S_{13} - S_{33}) \tag{2}$$

$$\left.\begin{aligned} &\kappa = S_{11} + S_{12} + S_{13}\,, \\ &S_{11} + S_{12} - S_{13} - S_{33} = 0\,. \end{aligned}\right\} \tag{3}$$

Accordingly, if κ can be measured, S_{12}, S_{13} and S_{44} will be determined from Eqs. (2) and (3). Bridgman[11], Slater[12], Schramm[13] and Tatsumoto[14] measured κ

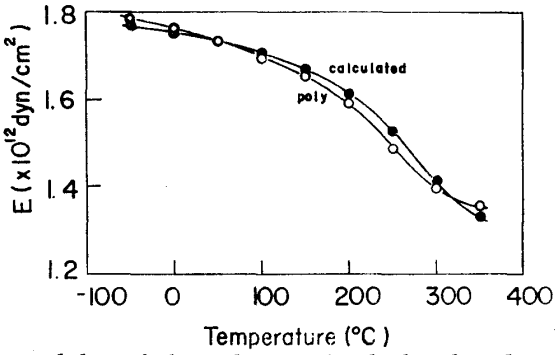

Fig. 9. Young's modulus of the polycrystal calculated and measured with the polycrystal specimen.

Table 3. Elastic anisotropy of cobalt single crystal at 20°C.

	Present investigators	Honda, Shirakawa
$\frac{E_{/}}{E_{\perp}}$	1.22	1.22
$\frac{G_{/}}{G_{\perp}}$	1.00	1.03

(10) K. Honda and H. Masumoto, Sci. Rep. Tôhoku Imp. Univ., **20** (1931), 323; H. Träbe, O. Baser, H. Kronmüller und A. Seeger, Phys. Status Solidi, **10** (1965), 283.
(11) P.W. Bridgman, Proc. Amer. Acad., **58** (1923), 165.
(12) J.C. Slater, Phys. Rev., **57** (1940), 744.
(13) K.H. Schramm, Z. Metallkde., **53** (1962), 316.
(14) M. Fujii, M. Tsurui, T. Kitai, T. Okamoto and E. Tatsumoto, Lecture at the 19th annual meeting of the Phys. Soc. Japan Oct. 5, 1964 (5aD3).

and gave a consistent value of 0.18×10^{-12} cm^2/dyn at room temperature. The variation in κ with temperature has been measured only by Tatsumoto in the temperature range −50° to 130°C. In the present case κ was obtained in the temperature range 130° to 350°C from the observed data by extrapolation, and the values for S_{12}, S_{13} and S_{44} shown in Fig. 6 were calculated. From these values, the principal elastic parameter C_{ij} can be calculated. The following equation will be valid between C_{ij} and S_{ij} for the hexagonal system[15].

$$\left.\begin{aligned} C_{11} &= \frac{1}{2}\left\{\frac{S_{33}}{S}+\frac{1}{S_{11}-S_{12}}\right\}, \\ C_{12} &= \frac{1}{2}\left\{\frac{S_{33}}{S}+\frac{1}{S_{11}-S_{12}}\right\}, \\ C_{13} &= -\frac{S_{33}}{S}, \\ C_{44} &= \frac{1}{S_{44}}, \end{aligned}\right\} \qquad (4)$$

where $S=S_{33}(S_{11}+S_{12})-2S_{13}^2$. The value of C_{ij} calculated from Eq. (4) is such as shown in Fig. 10, from which it is certain that Cauchy's relations, $C_{11}=3C_{12}$ and $C_{12}=C_{44}$[16], do not hold in the hexagonal system. The values of S_{ij} and C_{ij} at

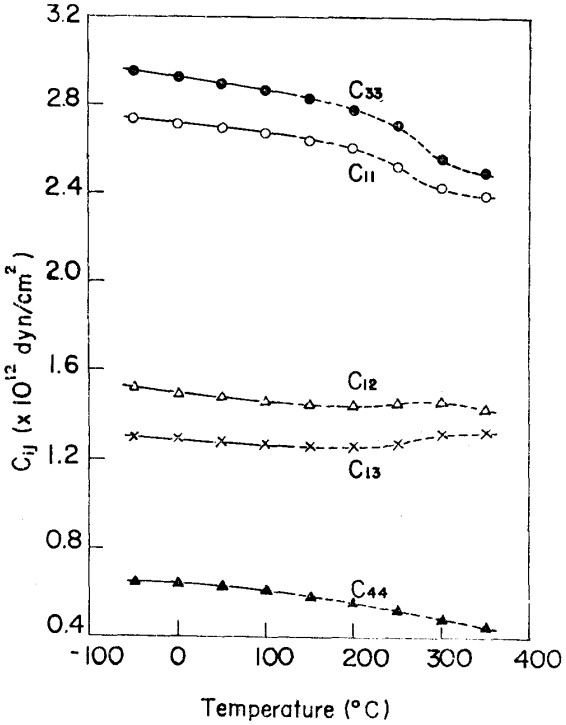

Fig. 10. Elastic constants of cobalt calculated with the elastic parameter S_{ij} shown in Fig. 6.

(15) W. Voigt, loc. cit., 747.
(16) For example; W. Voigt, loc. cit., 410.

Table 4. Elastic parameters S_{11}, S_{12}, S_{13}, S_{33} and S_{44} and elastic constants C_{11}, C_{12}, C_{13}, C_{33} and C_{44} at 20°C, calculated by the present and other authors.

S_{ij}	Present investigators	Honda, Shirakawa [1]	Mckskimin [2]
	($\times 10^{-12}$ cm²/dyn)		
S_{11}	0.572	0.622	—
S_{12}	− 0.246	− 0.277	—
S_{13}	− 0.143	− 0.163	—
S_{33}	0.469	0.508	—
S_{44}	1.584	1.928	—
C_{ij}	($\times 10^{12}$ dyn/cm²)		
C_{11}	2.708	2.63	3.071
C_{12}	1.485	1.52	1.650
C_{13}	1.280	1.33	1.027
C_{33}	2.912	2.83	3.581
C_{44}	0.631	0.52	0.755

20°C are listed in Table 4. As can be seen from the Table, the present results are not so much different from the data of Honda and Shirakawa, but show a considerable difference from the data of Mckskimin.

3. Rigidity modulus

For the hexagonal system, the rigidity modulus G can be expressed with S_{ij} as follows:

$$\frac{1}{G} = S_{44}\gamma^2 + \left(S_{11} - S_{12} - \frac{1}{2}S_{44}\right)(1-\gamma^2) + 2(S_{11} + S_{33} - 2S_{13} - S_{44})\gamma^2(1-\gamma^2). \quad (5)^{[15]}$$

By substituting the present values of S_{ij}, values of G in various orientations and at various temperatures were obtained as shown in Figs. 11 and 12. As in the case of E, it seems due to the differences in the specimen size and in the method of measurement that the values of G at room temperature obtained by Honda and Shirakawa are much smaller than those in the present case. The anisotropy of G, $G_{\parallel<0001>}/G_{\perp<0001>}$, is almost independent of temperature as shown in Fig. 11, except for a slight variation at about 260°C as in the case of E. The value is 1.0 in the vicinity of room temperature and somewhat different from that of Honda and Shirakawa as can be seen from Table 4, while the value at 350°C is 0.99. In Table 2 are shown the value of G at 20°C in the principal direction and the mean temperature coefficient g in the temperatures ranging from −50° to 200°C and 200° to 350°C.

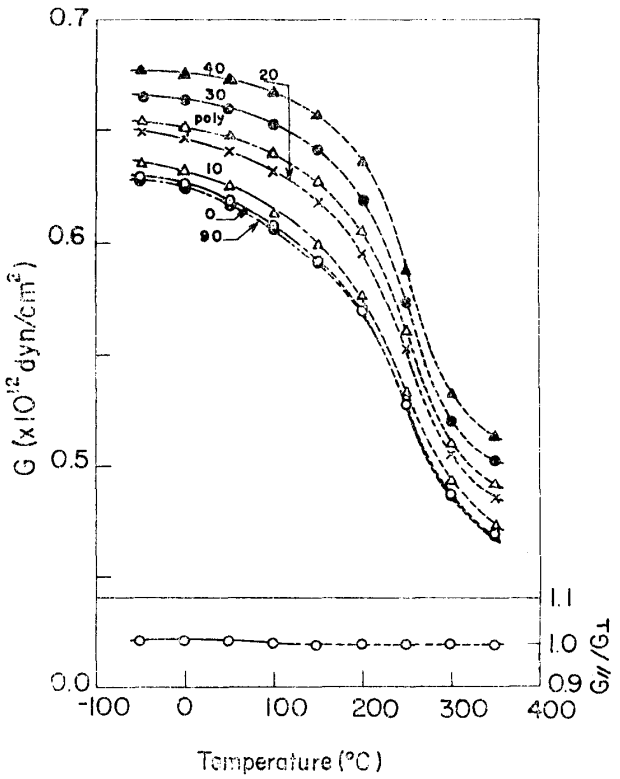

Fig. 11. Rigidity modulus G calculated with the elastic parameter S_{ij} and its anisotropy $G_{/\!/}/G_{\perp}$ of cobalt.

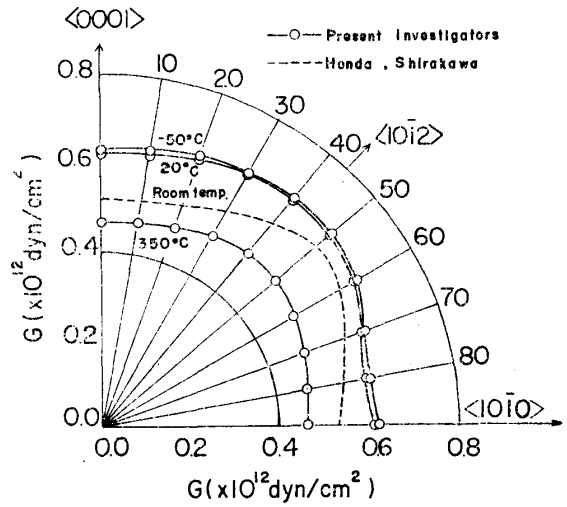

Fig. 12. Rigidity modulus G in the (10$\bar{1}$0) plane of hexagonal cobalt calculated with the elastic constant C_{ij} and the result of K. Honda and Y. Shirakawa[1].

IV. Conclusions

Cobalt single crystals were prepared in long cylindrical forms by Bridgman's method. The specimens were slowly cooled after heating at 350°C, and the thermal expansion and Young's modulus were measured in the temperature range from

−100° to 350°C. Then, the thermal expansion coefficient, Young's modulus and the rigidity modulus in various orientations were calculated from the measured values. The results obtained are as follows:

(1) The thermal expansion of the single crystal is almost linear in each orientation, and the calculated thermal expansion of the isotropic crystal is in good agreement with the measured one. The thermal expansion coefficient at room temperature is 14.62×10^{-6} in the orientation of c axis, 12.95×10^{-6} in the $\langle10\bar{1}2\rangle$ orientation and 10.97×10^{-6} in the perpendicular direction.

(2) Young's modulus at room temperature in the principal orientation is $E_{<0001>}=2.13\times10^{12}$, $E_{<10\bar{1}2>}=1.69\times10^{12}$, $E_{<10\bar{1}0>}=1.75\times10^{12}$ and $E_{<11\bar{2}0>}=1.74\times10^{12}$ dyn/cm^2. The calculated value at 20°C for the polycrystal is 1.75×10^{12} dyn/cm^2, in good agreement with the measured value.

(3) The temperature dependence of Young's modulus varies with orientation: the mean temperature coefficient is $e_{<0001>}=-52.10\times10^{-5}$, $e_{<10\bar{1}2>}=-74.60\times10^{-5}$, $e_{<10\bar{1}0>}=-33.55\times10^{-5}$ and $e_{<11\bar{2}0>}=-37.30\times10^{-5}$ at temperatures ranging over from −50° to 200°C, and $e_{<0001>}=-137.80\times10^{-5}$, $e_{<10\bar{1}2>}=-114.90\times10^{-5}$, $e_{<10\bar{1}0>}=-116.70\times10^{-5}$ and $e_{<11\bar{2}0>}=-118.82\times10^{-5}$ in the range 200° to 350°C. The curve of $E_{/\!/}/E_{\perp}$ shows a maximum at about 260°C, at which the sign of the magnetic anisotropy constant reverses. The calculated temperature dependence of Young's modulus of the polycrystal is almost consistent with the measured result.

(4) The principal elastic constant at room temperature is $C_{11}=2.708\times10^{12}$, $C_{12}=1.485\times10^{12}$, $C_{13}=1.280\times10^{12}$, $C_{33}=2.912\times10^{12}$ and $C_{44}=0.631\times10^{12}$ dyn/cm^2, from which it is clear that Cauchy's relation does not hold in cobalt.

(5) The rigidity modulus in the principal orientation at various temperatures and that for the polycrystal have been calculated. $G_{/\!/}/G_{\perp}$ is nearly independent of temperature, except for a slight variation at about 260°C, at which the sign of the magnetic anistoropy constant reverses.

Acknowledgements

The authors are indebted to Mr. Y. Sugai (At present, Sendai Precision Materials Laboratory Co., Ltd., Sendai) and staff members of the Specimen Preparation Laboratory in the Institute for their assistance and cooperation with experiments and computation. They also wish to thank Mr. S. Sawaya, the Foundation; The research Institute of Electric and Magnetic Alloys for the assistance of measurements.